

PATENT SPECIFICATION

NO DRAWINGS

1,030,003

1,030,003



Date of Application and filing Complete Specification May 31, 1963.

No. 22011/63.

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COMPLETE SPECIFICATION

Improvements in or relating to the Preparation of Cyclohexyl-Phenyl Ketone

ERRATA

SPECIFICATION No. 1,030,003

Amendment No. 1

Page 2, after line 130, insert "but the quantity of ketone formed is relatively"

Page 3, line 54, for "stream-" read "steam-"

Page 4, line 37, after "of" insert "the"

Page 6, line 9, for "hexyl-phenyl" read "hexylphenyl"

THE PATENT OFFICE

21st June 1966

25 no processes are known so far which permit the production of ketones in which the CO group is bonded to an originally secondary carbon atom, with quantitative yields.

30 For the production of ketones on industrial scale in general the corresponding acids are used as starting material. For instance ketones are obtained by distilling the alkaline earth salts of carboxylic acids. To produce mixed ketones a mixture of salts is used as starting material and in this case together with said mixed ketones there are always obtained the two corresponding symmetrical ketones (Houben-Weyl, 3rd Edition, Volume 3, page 530).

40 An attempt has been made to produce, in the same way, ketones in which the cyclohexyl radical is one of the radicals bonded to the carbonyl group. It is known, in fact,

Also by this method, from two different carboxylic acids, all three possible ketones are obtained. Only low yields are obtained from carboxylic acids wherein the CO group is bonded to an originally secondary carbon atom.

70 For the production of ketones containing a cyclohexyl radical adjacent to the carbonyl group, heretofore only laboratory methods have been available which for economic reasons are not appropriate for the industrial production of said ketones. Thus dicyclohexyl ketone is prepared by dehydrogenating the corresponding carbinol (C.A. 24,4286; Beilstein VII 143) and mixed ketones containing the cyclohexylic ring bonded to the carbonyl group are prepared by reacting cyclohexyl mercury with a corresponding acid chloride, for instance benzoyl chloride

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COMPLETE SPECIFICATION

Improvements in or relating to the Preparation of Cyclohexyl-Phenyl Ketone

We, SNIA VISCOSA SOCIETA' NAZIONALE INDUSTRIA APPLICAZIONI VISCOSA S.p.a. of Via Cernaia 8, Milan, Italy, an Italian Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the production of cyclohexyl phenyl ketone which in recent times acquired considerable importance as a raw material for the preparation of caprolactam. (see British patents No. 904413—904302—912034).

Cyclohexyl-phenyl ketone is a mixed ketone in which the CO group is bonded to a secondary carbon atom of a cycloaliphatic hydrocarbon radical as well as to a tertiary carbon atom of a phenyl radical. No methods are known so far which permit the exclusive production of the mixed ketones by processes that can be carried out on an industrial scale, and no processes are known so far which permit the production of ketones in which the CO group is bonded to an originally secondary carbon atom, with quantitative yields.

For the production of ketones on industrial scale in general the corresponding acids are used as starting material. For instance ketones are obtained by distilling the alkaline earth salts of carboxylic acids. To produce mixed ketones a mixture of salts is used as starting material and in this case together with said mixed ketones there are always obtained the two corresponding symmetrical ketones (Houben-Weyl, 3rd Edition, Volume 3, page 530).

An attempt has been made to produce, in the same way, ketones in which the cyclohexyl radical is one of the radicals bonded to the carbonyl group. It is known, in fact,

that by distilling barium acetate together with barium hexahydrobenzoate, cyclohexyl-methyl ketone is obtained in addition to dicyclohexyl ketone (Hell and Schaal, B.40, (1907) page 463). If only barium hexahydrobenzoate is distilled, dicyclohexyl ketone is obtained.

As is shown in the literature on both of these methods only unsatisfactory yields are obtained and the research work carried out by the applicants have confirmed that result (Hell and Schaal, B 40, (1907) page 4164).

Catalysts have been proposed for use in the production of ketones, e.g. metallic iron, thorium oxide and manganese oxide (Houben-Weyl, 4th edition, Volume IV/2, page 430; Sabatier and Mailhe, C. 1914, page 1640; C.r. 158 (1914) pages 830—835; C.A. 1960, 1280^b). As is shown in the literature, the ketones are obtained in the presence of these catalysts by passing the vapours of one or two different carboxylic acids over them at temperatures between 400° C. and 500° C. Also by this method, from two different carboxylic acids, all three possible ketones are obtained. Only low yields are obtained from carboxylic acids wherein the CO group is bonded to an originally secondary carbon atom.

For the production of ketones containing a cyclohexyl radical adjacent to the carbonyl group, heretofore only laboratory methods have been available which for economic reasons are not appropriate for the industrial production of said ketones. Thus dicyclohexyl ketone is prepared by dehydrogenating the corresponding carbinol (C.A. 24,4286; Beilstein VII 143) and mixed ketones containing the cyclohexylic ring bonded to the carbonyl group are prepared by reacting cyclohexyl mercury with a corresponding acid chloride, for instance benzoyl chloride

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(Beilstein, VII/II, 308) or by reacting a cyclohexylmagnesium halide (Grignard) with a carboxylic acid or its anhydride (C.A. 35,3980⁴). The most suitable method for the production of mixed ketones is still the Friedel-Crafts reaction. According to that method the chloride of hexahydrobenzoic acid is reacted with an aromatic hydrocarbon, for instance with benzene, in the presence of aluminum chloride. The yields of ketones obtained by this method are high. However, the industrial realization is rather difficult owing to the high consumption of aluminium chloride and owing to the necessity of preparing the starting material, i.e. the acid chloride.

Now it has been found surprisingly that from a mixture of hexahydrobenzoic acid and benzoic acid it is possible to obtain very pure cyclohexyl-phenyl ketone in substantially quantitative yields, by carrying out the ketonization in the presence of manganous oxide dissolved in the mixture of the two acids.

According to the invention there is provided a process for the production of cyclohexyl phenyl ketone comprising reacting benzoic acid and hexahydrobenzoic acid at temperatures between 280° C. and 450° C. in the presence of a catalyst comprising the manganous salts of said acids.

It has been found that manganous oxide at a temperature above 200° C. easily dissolves in the mixture of the two acids with formation of water. The mixture composed of one mole of hexahydrobenzoic acid and one mole of benzoic acid absorbs up to 1 mole of manganous oxide (MnO) and a transparent and limpid fused mass is obtained. The quantity of manganous oxide in excess of the molar ratio is not dissolved by the acids and remains suspended in the mass. Since manganous oxide is absorbed by the mixture in stoichiometric amounts with the formation of water, it may be supposed that after the dissolution of manganous oxide in the mixture, the salts of the corresponding carboxylic acids are present, though these have not been analyzed or exactly determined.

Therefore the solutions of manganous oxide in the mixture of the acids will be called hereinafter the manganese salts of the two acids.

In addition to the manganese salts that serve as catalysts, the molten mass may also contain some other metal oxides which under reaction conditions are substantially inert, but can form salts with the two acids. These metal oxides may bind a possible excess of the mixture of the acids, forming the salts, and may cede the mixture again to the catalyst if a deficiency of the acids should occur. Suitable metal oxides are for instance magnesium oxide or lithium oxide.

To carry out the process, the manganous oxide dissolved in the mixture of the two acids, which, may, moreover, contain other metal oxides, or the salts thereof formed with

said acids, and manganous oxide in suspension, is heated to temperatures at which CO₂ is developed with simultaneous formation of ketone which begins to distil.

To the catalyst there is added, continuously or portion-wise, a further quantity of the mixture of acid corresponding to that of the ketone formed. At the reaction temperature, the formation of the ketone proceeds regularly with simultaneous development of carbon dioxide and formation of water.

To obtain the mixed ketone exclusively, operation is carried out with a small molar excess of hexahydrobenzoic acid calculated on the benzoic acid. Said molar ratio should vary between 0.75 and 0.9 moles of benzoic acid for 1 mole of hexahydrobenzoic acid i.e. 0.1 to 0.3 moles of hexahydrobenzoic acid in excess per mole of benzoic acid. The excess hexahydrobenzoic acid is found unchanged in the distillate.

Operation can also be carried out with a greater excess of hexahydrobenzoic acid than indicated, which however does not provide any advantage. The distillate may also contain, depending on the method of operation a small quantity of unchanged benzoic acid.

The temperature at which the mixed ketone is obtained, can vary within wide limits. When the temperature of the molten mass which serves as a catalyst is kept between 280° C. and 420° C, the ketone is formed in abundance. If operation is carried out at a temperature near to the lower limit, the ketone formation per unit of time however is comparatively low. Operating at a temperature close to or higher than the maximum limit, the catalyst becomes exhausted rather quickly and the ketone obtained is not very pure.

The formation of the mixed ketone takes place with particular regularity at temperatures between 330° C. and 370° C.

The molar composition of the molten mass that serves as catalyst may vary within wide limits without any diminution of its activity. An efficient catalyst contains for instance 2 moles of a nearly equimolar mixture of hexahydrobenzoic acid and benzoic acid for about 1 mole of manganous oxide. Particularly efficient catalysts contain in general for 2 moles of mixture of the acids a slightly greater amount than 1 mole of manganous oxide, particularly an amount of 1.1 moles to 1.3 moles approximately. A catalyst of such composition is liquid at the reaction temperature and forms a molten mass containing manganous oxide in suspension.

If the operation is carried out with an excess of the mixture of acids, calculated on the totality of the metals present, the manganous oxide dissolves completely and a transparent molten mass is obtained. The ketone formation also takes place if the whole manganous oxide is dissolved in the molten mass,

small per unit of time. If the proportion of acids in the mixture is diminished by only a small amount in such a manner that in the molten mass somewhat less than 2 moles of acid are present per 1 mole of manganous oxide, a small quantity of manganous oxide separates out and remains suspended in the molten mass and the ketone formation proceeds very rapidly.

In general, at a constant temperature, a determined ratio between manganous oxide in suspension and manganous oxide dissolved in the molten mass, is obtained automatically. The quantity of manganous oxide dissolved is determined by the quantity of the mixture of acids which is present in the molten mass. At temperatures of from 330° C to 370° C, which are preferably applied for the formation of the ketone, a ratio of about 1 mole of manganous oxide per 1.6 to 1.9 moles of the mixture of acid is reached.

Using the catalyst for a longer time its efficiency diminishes, which besides other facts becomes noticeable by a variation of the ratio between the manganous oxide and the mixture of acids, even if the temperature is kept constant. If, for instance, at a temperature of 345° C. the initially reached ratio was about 1.9 moles of mixture of the acids per 1 mole of manganous oxide, the molar ratio after 24 hours' operation becomes 1.5:1. The yield is still substantially quantitative, but the conversion diminishes and the ketones which, in the presence of fresh catalyst are colourless, assume little by little a yellow colour.

It is also possible to operate even from the beginning with an excess of manganous oxide considerably larger than that corresponding to the ratio of about 1.7 moles of mixture of the acids per 1 mole of manganese. Also, in this case the ketone is initially obtained colourless, but it is more difficult to maintain for a long time a constant molar ratio between the mixture of the acids, and the manganous oxide.

It has been found, according to a feature of the present invention, that it is possible to keep the catalyst active for several weeks and to obtain a constantly colourless ketone, if the ketonization is carried out while steam is blown into the reaction mass. It is possible to introduce steam directly into the molten mass that serves as a catalyst, or to steam-distil the mixture of acids thus introducing steam and mixture of the acids simultaneously.

In the presence of steam the ratio between the manganous oxide and the acids present in the molten mass varies only a little even after a long period of operation. The preparation of the catalyst may be carried out in various ways. For instance, 2 moles of a mixture containing benzoic acid and hexahydrobenzoic acid in a molar ratio of 1:1 to 1:1.2, are slowly heated with stirring up to 280° C.

together with 1.1 to 1.4 moles of manganese carbonate, firstly in a reflux condenser and then in a downward condenser, until the development of carbon dioxide and the formation of water have substantially ceased. In lieu of manganese carbonate, the corresponding quantity of manganous oxide may be employed, or the catalyst may even be prepared by double transposition of aqueous solutions of the salts of the two organic acids with manganese salts soluble in water.

If the ketonization is carried out in the presence of a metal oxide which is inert with respect to the reaction mixture, for instance in the presence of magnesium oxide, the catalyst is prepared by adding an additional amount of the mixture of acids equivalent to the quantity of magnesium oxide present.

The production of cyclohexyl-phenyl ketone may be carried out by various methods; such methods, however, are carried out in all cases in the presence of the salts of the two acids used as the starting material, as hereinbefore described. It is possible, for instance, to operate at normal pressure as well as under vacuum or at elevated pressure.

Also, the mixture of hexahydrobenzoic acid and benzoic acid to be transformed into ketone can be introduced, by various methods, into the molten mass that serves as a catalyst. For instance, it is possible to introduce it into the stirred molten mass while continuously blowing in small amounts of steam.

In lieu of introducing the mixture of acids continuously, it is possible also to add it in portions. Operating in this way, the temperature of the molten mass falls at each addition in dependence on the quantity introduced, whereafter heating is continued until a quantity of ketone, equal to the quantity of the mixture of acids added is formed.

According to another method of operation, the molten mass of the catalyst is made to pass by means of a pump maintained at the required temperature, through a tube kept at the reaction temperature and, the molten or vaporized acids are introduced at a suitable point, into the apparatus.

The salts ought to derive from the bivalent form of manganese; therefore it is advisable to carry out the ketonization by introducing small quantities of hydrogen in order to avoid the oxidation of manganous oxide.

Operating correctly there is obtained, surprisingly the mixed ketone in a yield of more than 98% calculated on the reacted acids. The ketone obtained is sufficiently pure to be utilized for other purposes or chemical reactions, provided that the acids still present, do not interfere. If necessary it is possible to separate them by filtration or centrifugation, from the ketone, which crystallizes very easily at room temperature.

The catalyst remains active for a long time,

especially in the presence of steam, and the consumption of manganous oxide, which can be regenerated by one of the known methods, is not higher than 0.1 to 1%, calculated on the ketone produced.

5 In the course of the reaction there are formed in molten mass which serves as a catalyst, small quantities of resinous products which do not, however, exceed 0.1% calculated on the ketone formed.

10 By operating according to the same method, but replacing the manganous oxide by ferrous oxide or cadmium oxide, also the mixed ketone is again obtained, but the yields are not quantitative and vary between 40% and 85% of the theoretical yield calculated on the reaction mixture of the acids.

Many resins and many secondary products are formed and the catalysts quickly become

20 inactive. The invention will be better understood by the following non-limiting Examples.

EXAMPLE 1

25 In a 2 litre flask, provided with a stirrer, thermometer, inlet for the introduction of gas, dripping funnel and reflux condenser, there are mixed while stirring at 81° C, 524 g of commercial manganese carbonate containing water (manganese content 42% = 4 gram atoms) with 270 g (2.2 moles) of hexahydrobenzoic acid and 210 g (1.8 moles) of benzoic acid. The mixture is heated to 122° C for 1 hour, and CO₂ and water are formed.

30 The reflux condenser is replaced by a downward condenser.

35 To the mass in the flask is slowly added a quantity of acid mixture equal to that already charged and, while stirring, the temperature is raised to 340° C over a period of two and a half hours.

40 The formation of the ketone begins at 280° C and becomes vigorous at 340° C.

At that time, the contents of the flask weighs 1180 g.

45 Heating is continued until the temperature reaches 345° C and, while stirring, a fresh mixture of hexahydrobenzoic acid and benzoic acid (molar ratio of 1.22:1) made molten by slight heating (81° C), is added slowly by means of the dropping funnel and at the same time a slight stream of hydrogen is passed through the reaction mass. While the water and the ketone distil, a regular stream of the CO₂ formed, together with the hydrogen, escapes.

50 Introducing 340 g of the mixture of acids per hour, into the reaction mixture an almost colourless product continuously distils, which, slowly assumes a yellow colour if the operating time is extended.

60 To calculate the conversion and yield the reaction is interrupted after 24 hours. At that time the distillate containing water weighs 7335 g. A residue of 952 g remains in the

65 flasks which with respect to the weight of 1180 g found at the beginning of the ketone formation, indicates a loss of weight of 228 g equalling 19.6%.

70 To separate the ketone, the distillate is diluted with ether. The acids contained in the distillate are extracted with a 10% aqueous solution of sodium carbonate and the aqueous layer is separated. After acidifying and subsequently distilling the crude mixture of the separated acids, there are obtained 1695 g of a mixture of pure acids, composed of 76.5% of hexahydrobenzoic acid and of 23.5% of benzoic acid, as shown by the refractometric test.

80 The organic layer is dried, the ether is removed and the residue is distilled at 0.1 mm Hg. At the beginning (76 to 78° C), cyclohexylphenyl ketone distils, which contains traces of dicyclohexyl ketone (refractometric test). At 80—81° C, pure cyclohexyl-phenyl ketone distils and finally (81—84° C) cyclohexyl-phenyl ketone distils containing traces (0.2%) of benzophenone (refractometric test). There remains a residue of 24 g partly formed by resins and partly by ketone. Thus 5005 g of cyclohexyl-phenyl ketone are obtained.

90 The mass remaining in the reaction vessel is heated with an excess of hydrochloric acid until the manganese has dissolved as chloride in water and the aqueous layer is separated from the organic layer which is treated as already described for the distillate.

95 80 g of cyclohexylphenyl ketone, 591 g of the acid mixture containing hexahydrobenzoic acid and benzoic acid in the molar ratio 51.3:48.7%, and 26 g of residue are thereby obtained. Taking into account the introduced quantity of 9120 grammes of acids including the 960 g employed for the preparation of the catalyst, and the overall quantity of 2286 g recovered, including the 591 g recovered from the catalyst, the total yield of cyclohexylphenyl ketone is 5085 g., that is to say, 98.35% of the theoretical yield. The conversion of benzoic acid is calculated on the basis of the ratio between ketones deriving from benzoic acid, and the non-reacted benzoic acid contained in the distillate. The quantity of ketones, 5005 g, contained in the distillate corresponds to 3284 g of benzoic acid. Furthermore in the distillate there are still 398 g of non-reacted benzoic acid; the conversion of benzoic acid is therefore 87.5%.

100 105 110 115 120 125 If operation is carried out with the same quantities indicated above, but with a modified apparatus, introducing the mixture of the acids into the molten mass forming the catalyst from below, instead of dropping it from above, and keeping the apparatus under a vacuum of 140 mm Hg, the conversion increases by about 2.6% and, therefore, attains 90.1%. If operation is carried out in an autoclave, closing it every time before proceeding

with the introduction of the mixture of acids, and opening it when the temperature has attained 340° C.—leaving it open until the CO₂ has completely escaped and the water and an amount of organic substance equivalent to that of the acids introduced are distilled off—there is obtained a conversion of the benzoic acid equal to 97% and a yield of ketone equal to 97% of the theoretical yield.

10 EXAMPLE 2

As described in Example 1, 524 g of commercial manganese carbonate (=4 moles of manganese) are mixed with 740 g of hexahydrobenzoic acid (=5.78 moles) and 576 g of benzoic acid (=4.72 moles) and heated slowly to a temperature of 280° C. Carbon dioxide and water are formed and a completely clear molten mass is obtained.

While the temperature is slowly raised to 340° C without adding any acid, a ketone is formed with simultaneous development of CO₂. At 340° C. the formation of the ketone becomes more vigorous and, because MnO separates and remains in suspension, the molten mass assumes a green colour.

Introduction of 47 g per hour of steam into the molten mass is started. The temperature of the molten mass is raised to 345° C. and while maintaining this temperature, an overall amount of 9728 g of the acid mixture (molar ratio 1.226:1) is introduced. Carbon dioxide is formed and ketone and water distil.

After having introduced an overall amount of 11044 g of the acid mixture (containing 4946 g of benzoic acid), the process is interrupted. The distillate and the mass that remains in the reactor, are treated as described in Example 1.

From the distillate are recovered 2393 g of the acid mixture and 5822 g of cyclohexyl-phenyl ketone are obtained. From the mass that remains in the reactor a further 736 g of the acid mixture and 65 g of cyclohexyl-phenyl ketone are obtained.

The overall yield of cyclohexyl-phenyl ketone amounts to 5887 g, equal to 98.9% of the theoretical yield, taking into account the 3129 g of acids recovered.

Owing to the presence of steam the colour of the molten mass that serves as catalyst is much clearer, even after 24 hours' operation, compared to that of Example 1.

In fact, after the normal treatment it appears that the content of resinous products is only about 10 grammes compared with more than double that amount obtained if operation is carried out according to Example 1. Also, after prolonged use and even for the duration of one week the catalyst keeps its full activity and substantially colourless ketone is obtained. Moreover the losses in weight of the molten mass that serves as a catalyst is

much smaller after, for instance 28 hours' operation.

In fact, the quantity of 1180 g being in the reactor at the beginning of the ketone formation diminishes to 1080 g (9.6%) only, while the weight of the molten mass that serves as a catalyst diminishes by only 20% after 24 hours if operation is carried out without steam, as described in Example 1.

In this case the conversion of benzoic acid is slightly lower (85.1%), due to the fact that a part of the acid is dragged away by the steam before reacting.

EXAMPLE 3

524 g of commercial manganese carbonate (=4 moles of manganese) and 80.6 g of magnesium oxide (2 moles) are mixed with 845 g of hexahydrobenzoic acid (=6.6 moles) and 659 g of benzoic acid (=5.4 moles) and the mixture is heated while stirring and refluxing for 1 hour to a temperature of 125° C. Carbon dioxide and water are formed. The reflux condenser is replaced by a downward condenser, 45 g of steam per hour are passed through the molten mass formed, which, while stirring is slowly heated to 340° C over a period of two and a half hours.

150 g portions of a mixture fluidized by heating it to 81° C containing hexahydrobenzoic acid and benzoic acid in a molar ratio of 1.2:1, are added.

After every addition the temperature of the mass falls by about 35° C. After 15 minutes the temperature is restored to 340° C. Carbon dioxide develops and simultaneously water and ketone distil. In that way the process can be carried on for a long time.

After the interruption of the process, the reaction mixture and the residue in the flask are treated as described in Example 1.

Taking into account the quantities of acids recovered, there is obtained a yield of cyclohexyl-phenyl ketone that is nearly quantitative and averages 99.5% of the theoretical yield.

The conversion of benzoic acid is slightly higher than that obtained by the tests carried out in the absence of magnesium oxide, and attains about 93% on an average.

WHAT WE CLAIM IS:—

1. A process for the production of cyclohexyl phenyl ketone comprising reacting benzoic acid and hexahydrobenzoic acid at temperatures between 280° C. and 450° C. in the presence of a catalyst comprising the manganous salts of said acids.

2. A process as claimed in claim 1, wherein there is an excess of 0.1—0.3 moles of hexahydrobenzoic acid in relation to the benzoic acid.

3. A process as claimed in claim 1 or claim 2, wherein the mixture of the manganous salts of the two acids serving as catalyst, contains manganous oxide in suspension.

4. A process as claimed in claim 1, claim 2 or claim 3, wherein the reaction is carried out with the introduction of steam into the mixture of reactants.
- 5 5. A process as claimed in any preceding claim, wherein the reaction is carried out in the presence of a small quantity of hydrogen.
6. A process for the production of cyclohexyl-phenyl ketone as set forth in any of the foregoing Examples.
- 10 7. A process for the production of cyclohexylphenyl ketone as claimed in claim 1, substantially as described herein.
8. Cyclohexyl-phenyl ketone when prepared by the process as claimed in any of the preceding claims.
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